Some Recent Topics in Gold Plating for Electronics Applications

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A review is presented of selected recent topics in electrolytic and electroless gold plating for electronics applications. The topics covered include developments of non-cyanide electroplating baths for plating soft gold suitable for fabricating microbumps on silicon wafers, electroplating of hard gold and alternative materials with thermally stable electrical contact resistance and wear resistance for use on connectors exposed to elevated temperatures, and neutral, non-cyanide electroless processes for plating pure, soft gold on isolated areas of circuit boards. The development of the new electroless processes has been a subject of great interest and activity, and therefore an extensive survey of the progress in this field is included.

The electroplated gold being used in the electronics industry can be broadly classified into soft gold and hard gold. Soft gold is used as a surface finish for bonding gold or aluminum wire in the conventional method of mounting semiconductor devices on a circuit board. In more recent years, with the advent of the so-called surface mount technology, the wire bonding has been replaced by the direct bonding of microbumps fabricated on silicon wafers by the electroplating of soft gold. Since the bonding of a large number of bumps is involved for each chip, uniformity in the bump geometry is important. The gold must be sufficiently soft so that the bumps are easily deformable to accommodate small variations in thickness. Photolithography is employed to delineate patterns for the formation of bumps. Conventional photoresists are attacked by the cyanide which is present in ordinary soft gold plating baths. Consequently, non-cyanide baths must be used for this purpose.

Hard gold is used on electrical connectors and contacts requiring resistance to mechanical wear as well as low electrical contact resistance. The gold is electroplated from a bath containing potassium cyanoaurate(I), $KAu(CN)_2$, as the source of gold and a salt of cobalt, nickel, or iron as the hardening agent. With the recent trend of miniaturization and densification of electronic parts and components, connectors also tend to become smaller in size with a larger number of individual connector pins or sockets. As a result of this trend, the magnitude of current passing through an individual pin/socket pair is increased in some applications, resulting in a rise in temperature at the mating surfaces. Exposure to elevated temperature is also encountered during the soldering operations performed to attach cable wires to connectors. The extent of the temperature rise at the contact surface is greater for connectors with smaller pins because of the proximity to the area to be soldered. Under these circumstances, it is important that the electrical resistance of the contact material remains low and stable at elevated temperatures. Thermal stability is also critical in applications for the electronic equipment used in automobiles.

Electroless gold plating is unique in that it requires no external source of electrical current, and hence it is suitable for plating gold on electrically isolated areas, for example, on a circuit board. It should be noted that

the term 'electroless plating' is often used to describe three fundamentally different processses: galvanic displacement, substrate-catalysed, and autocatalytic processes. In the first two procceses, the plating reaction should cease when the substrate is covered completely with gold. In the autocatalytic process, the plating should continue indefinitely, and hence this technique is more suitable for obtaining a thick, non-porous layer of gold. Classical autocatalytic gold plating baths contain excess cyanide, and they are operated at a high pH; and they are not therefore compatible with conventional positive photoresists. Non-cyanide baths operated at a neutral pH have, however, been developed in recent years, and they are now commercially available.

In the sections which follow, the topics briefly mentioned above are reviewed, and areas requiring further improvements discussed.

This review is intended to supplement the recent article by Christie and Cameron (1), which covers more general aspects of gold plating technologies and their applications.

SOFT GOLD

The conventional cyanide bath for electroplating soft gold has been extensively studied in the past, and a considerable amount of information on various aspects of the process, deposit properties, and microstructure is available in the literature (2-4). The knowledge acquired for the cyanide system has been applied to a great extent to the recent development of non-cyanide systems. In this section, only the non-cyanide systems will be described.

Sulfite Baths

The use of a gold sulfite complex for gold plating has been known since 1842 (2), and it is still the gold complex most commonly used to prepare non-cyanide baths. Gold sulfite baths traditionally attracted attention because of their ability to produce smooth, bright, and ductile pure gold deposits with good microthrowing power. Gold alloy deposits of low or high carat with high ductility can also be produced more readily with sulfite baths than with cyanide baths (2, 3).

In the sulfite baths, gold exists in the form $[Au(SO_3)_2]^{3-}$. The stability constant of this complex is approximately equal to 10^{10} (5), which is orders of magnitude smaller than that of the cyanide complex, $[Au(CN)_2]^-$, ie 10^{39} (6). For this reason, the sulfite complex tends to decompose spontaneously to form a precipitate of metallic gold *via* the following disproportionation reaction:

$$2Au^+ \longrightarrow Au(0) + Au^{3+} \qquad (1)$$

To suppress the bath instability resulting from this reaction, all commercially available sulfite baths contain proprietary stabilizing additives. The addition of an amine such as ethylenediamine is well known to stabilize the bath through the formation of a mixed gold complex (2, 3). More recently, Honma and Kagaya (7) found that the addition of 2,2'-dipyridine suppresses the disproportionation reaction to a large extent, presumably through the formation of its complex with Au^+. No adverse effect was observed on hardness or surface morphology.

It should be noted that many Au(I) sulfite baths described in the literature are operated at a pH equal to or higher than 8.0 (2, 3, 7). Since conventional positive photoresists are unstable in the alkaline pH range, it is desirable to use a bath that can be operated at a neutral or acidic pH. The addition of ethylenediamine makes it possible to operate the bath in the pH range of 5 to 8 (3). Furthermore, as described by Morrissey (8), simultaneous addition of both a polyamine such as ethylenediamine and an aromatic nitro compound such as nitrobenzene stabilizes the Au(I)-sulfite complex to such an extent that the bath can be operated at a pH as low as 4.0 to 6.5.

The addition of As^{3+} improves the brightness of the gold deposit, but it is known to increase its hardness if the bath is operated at an alkaline pH (7, 8). With the acidic bath of Morrissey, the addition of As^{3+} improves the brightness without increasing the hardness.

Thiosulfate Bath

The electrodeposition of gold from an Au(I)-thiosulfate complex has been known since as early as 1913 (3), but it has never been used for making a practical plating bath. The stability constant of the $[Au(S_2O_3)_2]^{3-}$ complex is equal to 10^{26} (9), which is substantially greater than that of the sulfite complex, *ie* 10^{10}. Thus, the thiosulfate complex might be expected to be a viable alternative to the sulfite complex. The reason why the thiosulfate complex has not been successfully used for making a practical gold plating bath seems to be the instability of thiosulfate ion itself with respect to Reaction (2):

$$S_2O_3^{2-} \rightleftharpoons S + SO_3^{2-} \qquad (2)$$

The forward reaction liberates elemental sulfur. The mixed ligand system containing both sulfite and thiosulfate, which is described in the following section, was investigated as a consequence of the stabilizing effect of SO_3^{2-} anticipated from the above equilibrium.

Thiosulfate-Sulfite Mixed Ligand Bath

Osaka and coworkers (10) recently investigated the possibility of electroplating soft gold from a thiosulfate-sulfite mixed ligand bath, specifically for application to the formation of microbumps on silicon wafers. Optimized bath compositions and operating conditions are listed in Table 1 together with the hardness values of the gold deposits obtained. This bath is operated at a slightly acidic pH of 6.0 and at a mildly elevated temperature of 60°C. It is highly stable, and there is no need to add any stabilizer to suppress spontaneous decomposition. The gold plated under optimal conditions has a Vickers hardness of approximately 80 kg mm^{-2} in the as-deposited state, which decreases to 50 kg mm^{-2} upon annealing at 350°C for only 30 min.

As mentioned already, the gold to be used as bumps should be as soft as possible. The addition of thallium ions has been shown to be an effective means of decreasing the hardness as well as improving the appearance of the gold deposit. Furthermore, it has been shown that increasing the concentrations of thiosulfate and sulfite also decreases the hardness significantly. Results of analyses of impurity elements included in the gold revealed that both the addition of thallium ions and the use of a high ligand concentration significantly decrease the sulfur content of the gold deposit. It has been established that the hardness and the sulfur content are directly related to each other. These relationships are illustrated in Figures 1 and 2. On the other hand, a microstructural study showed that the size of individual crystals of gold is larger for the softer gold containing less sulfur. All of these findings are reminiscent of the effects of various factors on the hardness of soft gold plated in the conventional cyanide bath, where the impurity content, as represented by carbon, is directly related to the hardness (11).

Table 1 *Compositions and operating conditions of gold(I) thiosulfate-sulfite mixed ligand bath and Vickers hardness of electroplated soft gold*

	With Tl^+	Without Tl^+
$NaAuCl_4 \cdot 2H_2O$	0.06 M	0.06 M
Na_2SO_3	0.42	1.1 - 1.4*
$Na_2S_2O_3 \cdot 5H_2O$	0.42	1.1 - 1.4*
Na_2HPO_4	0.30	0.30
Tl^+(added as Tl_2SO_4)	5 ppm	-
pH	6.0	
Temperature	60°C	
Current density	5 mA cm^{-2}	
Agitation	mild	
Deposit hardness (kg mm^{-2})		
As deposited	88	87-88
After annealing at 350°C	52	45-60

* $[Na_2SO_3] : [Na_2S_2O_3] = 1 : 1$

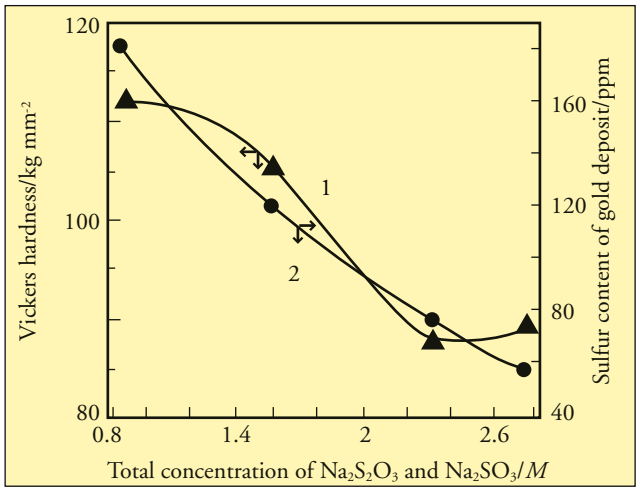

Figure 1 *Effect of total ligand concentration ($Na_2S_2O_3$+Na_2SO_3) on hardness (curve 1)and sulfur content (curve 2) of electroplated soft gold deposit. ($[Na_2S_2O_3] : [Na_2SO_3] = 1 : 1$; no Tl^+ ; for concentrations of other bath constituents and operating conditions, see Table 1) (from reference 10)*

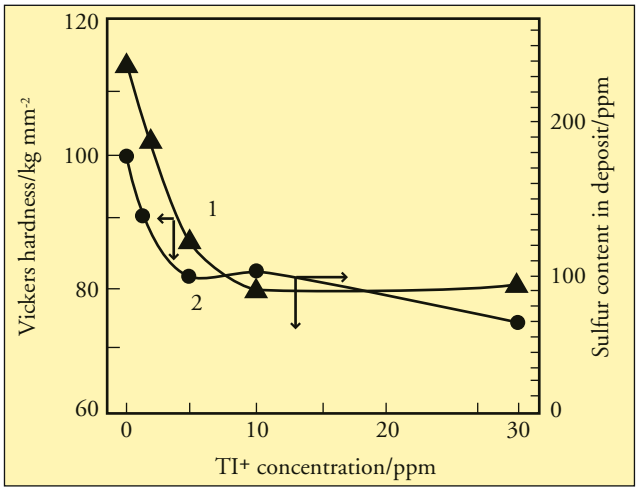

Figure 2 *Effect of thallium ion concentration on hardness (curve 1) and sulfur content (curve 2) of electroplated soft gold. (For concentrations of other bath constituents and operating conditions, see Table 1) (from reference 10)*

Figures 3(A) and 3(B) are SEM photographs of 20 micrometer thick bumps plated in the mixed ligand bath before and after removal of photoresist, respectively. It is seen that the bump walls are straight, indicating that no deterioration of the photoresist took place during the plating.

HARD GOLD AND ALTERNATIVES

Hard gold plating baths containing $KAu(CN)_2$, citrate buffer, and a small amount of Co^{2+} or Ni^{2+} ions, which are operated at an acidic pH of about 4, were described in the late 1950's (2). They are still being used extensively by the connector manufacturing industry. A majority of connector contacts are plated with Co-hardened gold (CoHG). The plating process and deposit properties of this type of gold have been thoroughly investigated over a period of many years, and they have been reviewed in great detail (2-4, 12). The compositions and operating conditions of the baths can be found in commonly available books and review articles, and they will not be reproduced here.

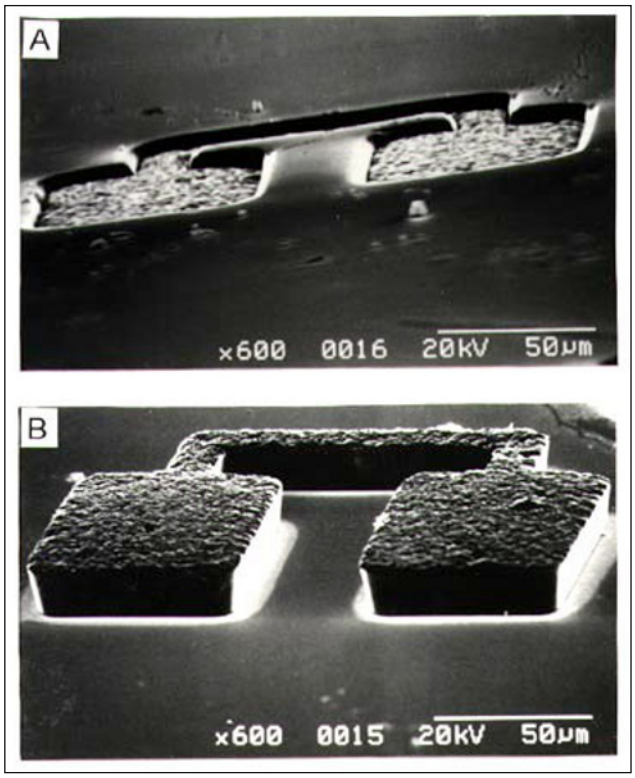

Figure 3 *SEM photographs of gold bumps on silicon wafer produced from thiosulfate-sulfite mixed ligand bath with a total ligand concentration of 2.28M and no Tl^+. (A) before, and (B) after photoresist removal (from reference 10)*

Hardness and Wear Resistance

The hard gold contains less than 0.4% by weight of Co or Ni, and yet the deposit hardness (170-200 kg mm^{-2} in Knoop hardness) is more than twice as high as that of soft gold deposits (70-80 kg mm^{-2}). Gold-cobalt or gold-nickel alloys with such high hardness values cannot be produced by incorporating such small amounts of the base metals using traditional metallurgical methods. The study of the hardening mechanism performed by Lo, Augis, and Pinnel (13) shows that the major factor determining the hardness is the grain size. The hard gold deposits consist of extremely small grains measuring 20-30 nm, compared to 1-2 µm for soft gold. It has been shown that hard gold can be plated even without any hardening additives (14, 15) if the bath is operated under a suitable set of current density and temperature conditions. The grain size of the additive-free hard gold (AFHG) is comparable to that of CoHG or Ni-hardened gold (NiHG) (16).

The decreased grain size of the hard gold is believed to be due to the inhibition of crystal growth brought about by incorporated impurities or inclusions. The classical work by Raub and coworkers (17-19), describing the effects of plating variables on the inclusion of various elements is well known. Examples of impurity contents of CoHG, AFHG, and soft gold are listed in Table 2 in terms of ppm by weight for various elements. Considerable efforts were made in the past to establish the chemical identity of included compounds, but the identification has so far been incomplete. Two compounds, AuCN and $K_3Co(CN)_6$, have been identified, but they do not account for the presence of a large excess of carbon over nitrogen. It is not known in what form the hydrogen exists in the gold. Nevertheless, it seems clear that the inclusions play a highly significant role in determining critical physical properties of hard gold:

Table 2 *Examples of impurity contents of cobalt-hardened gold (CoHG), additive-free hard gold (AFHG), and soft gold (SG) (ppm by weight)*

Impurity elements	CoHG	AFHG	SG
C	2800	550	~10
H	405	95	–
O	927	–	–
N	1720	300	–
K	2750	2200	_

(The dash sign (–) indicates data not available)

ie, wear resistance and electrical contact resistance. The CoHG, which contains much greater amounts of impurity elements than AFHG, has a considerably better wear resistance than the latter (14, 15), in spite of the fact that both types of gold have a similar hardness. Obviously, hardness is not the only factor controlling wear resistance. The CoHG contains cobalt in two different forms: complexed Co in the form of $K_3Co(CN)_6$ and metallic Co. It has been shown that good wear resistance is obtained only with a sufficient amount of complexed Co (>0.08 wt%) present in the gold together with 0.06-0.2 wt% of metallic Co (20). Various proposals have been made to explain why CoHG has good wear resistance. Its low ductility (21) and high internal stress (22) were thought to be relevant. However, the reason for the good wear resistance of CoHG is not yet fully understood.

Contact Resistance

Low and stable electrical contact resistance is another important property required of the contact material used on connectors and switches. It is recognized that the contact resistance of CoHG can increase to an unacceptable level at elevated temperatures, depending on the cobalt content of the gold. A study performed by Thomas and Sharma (23) shows that cobaltous oxide, CoO, is formed on the surface of CoHG. The work reported by DeDoncker and Vanhumbeeck (20) indicates that the contact resistance is determined by the content of metallic Co rather than that of complexed Co. Obviously, the CoO forms as a result of the oxidation of metallic Co, not complexed Co.

More recently, Huck (24) compared the contact resistance stability of CoHG and NiHG at elevated temperatures. With 1.5 to 2.0 μm thick films the contact resistance of both CoHG and NiHG was low and stable at <10 milliohms for 1500 hr at 125°C; whereas after 1500 hr, the contact resistance of CoHG began to increase much more rapidly than that of NiHG. At 300°C, the contact resistance of CoHG began to increase, after only one minute, much more quickly than that of NiHG. These results are reproduced in Figure 4. Auger spectroscopic analyses of the surfaces of CoHG and NiHG heat-treated at both 125 and 300°C showed that Co and Ni are both segregated on the surfaces to a similar extent. The reason why CoHG has a higher contact resistance than NiHG after the heat treatment may be that the cobalt oxide is less conducting than nickel oxide. In Table 2 it is seen that both CoHG and AFHG contain a significant amount of potassium. Huck found that at 300°C, the potassium is segregated considerably on the surface of both CoHG and NiHG. The significance of this finding is not clear at present. The thickness of the segregated surface films has been reported to be less than 0.01 μm. The investigation performed by Huck clearly demonstrates that NiHG is superior to CoHG as far as the thermal stability of contact resistance is concerned.

Alternative Materials

Alternative contact finishes to replace or save gold began to be evaluated in the late 1970's when the cost of gold escalated to an excessive level. Palladium and its alloy with nickel capped with a thin layer of CoHG (0.1μm) have been investigated extensively for this purpose, and they now have a history of successful use

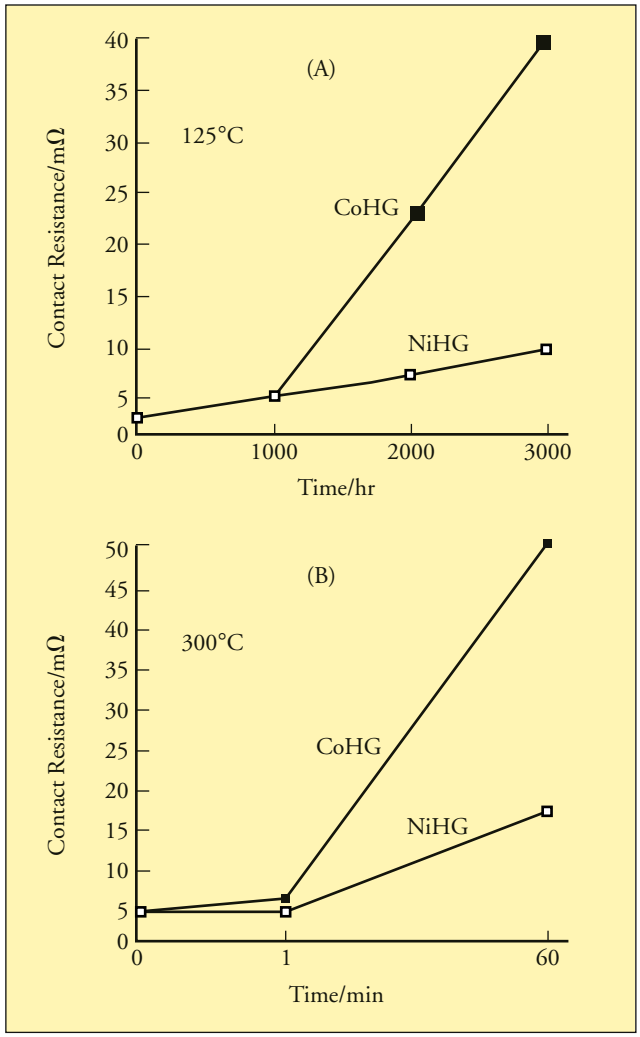

Figure 4 *Schematic comparison of contact resistance stability of cobalt-hardened gold (CoHG) and nickel-hardened gold (NiHG) at (A) 125°C and (B) 300°C (data points represent average values reported by Huck (24))*

for more than 15 years. These materials were considered initially only for economic reasons, but their technical advantages over hard gold are now clearly recognized. One advantage results from the high hardness of electroplated palladium (300-325 kg mm^{-2} in Knoop hardness) compared to that of hard gold (130-200 kg mm^{-2}), implying a greater wear resistance of palladium. This aspect was evaluated quantitatively by Kudrak *et al* (25) by comparing results of wear tests performed on connector contacts, which were plated with hard gold and gold-flashed palladium, respectively. Their results of surface analysis carried out after different numbers of insertion-withdrawal cycles demonstrate that the wear resistance of gold-flashed palladium is superior to that of the conventional CoHG.

As mentioned already, thermal stability of contact resistance is an increasingly important attribute for contact materials in recent years. Small connectors with a large number of contact pins are frequently required. Connectors with pin widths and intervals as small as 0.5 to 0.8 mm are now in use. A photograph showing such small pins and connectors is presented in Figure 5. For applications of these connectors on surface-mount boards, the contacts are required to withstand temperature excursions up to 240°C, which is a solder reflow temperature.

Exposure to elevated temperatures is also encountered in connectors used in automobiles. Gold-flashed pure Pd and gold-flashed Pd-Ni alloy are increasingly being used as contact finishes for this application because of their superior contact resistance stability at elevated temperatures as compared to CoHG or NiHG. Kudrak *et al* (26) compared performances of various contact finishes specifically for automobile applications. It was noted that in those applications, contact finishes must withstand exposure to 150 to 200°C, and in some cases up to 350°C. The CoHG is generally recognized to be unsuitable for this type of application. Even NiHG exhibited an unacceptably high contact resistance after 2000 hr at 200°C. Gold-flashed Pd-Ni alloy contacts showed a significant increase in contact resistance within 500 hr at the same temperature, whereas gold-flashed pure Pd

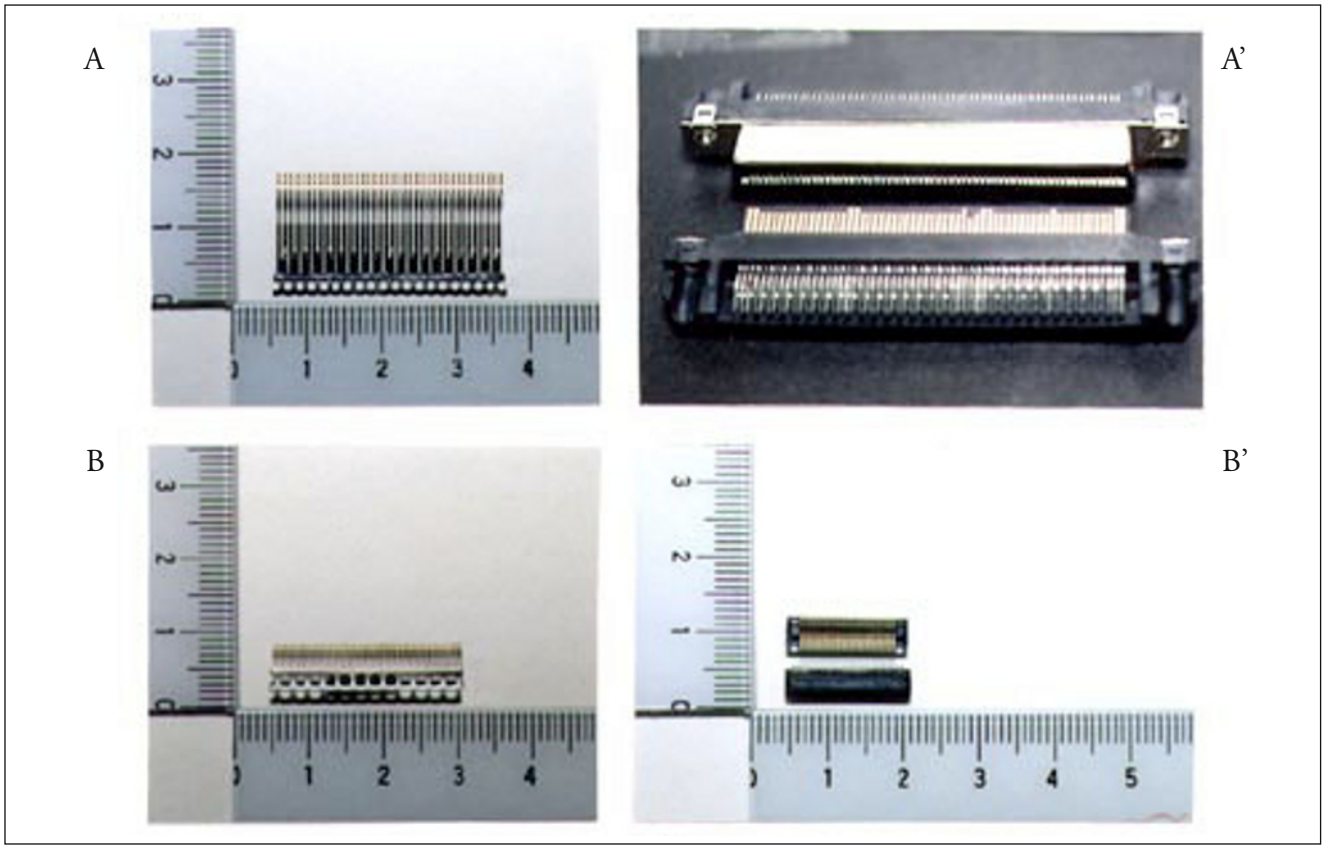

Figure 5 *Photographs of (A, B) high density connector pins selectively plated with CoHG and (A',B') assembled connectors. (A,A': 13 pins/cm, B,B' : 20 pins/cm. B' shows a connector for a surface-mount circuit board)*

showed little increase within 1000 hr, but a noteworthy increase after 2000 hr. The most superior finish was found to be a gold-flashed multilayer finish (proprietary), which exhibited no changes in contact resistance in up to 2000 hr. These results indicate that the conventional CoHG and NiHG do not meet recent requirements for thermal stability of connector contacts which are to be exposed to temperatures above 200°C for any extended period of time. Palladium-based contacts are expected to find an increasing number of applications in this area. It should be remembered that the presence of a thin (0.1μm) top layer of CoHG is critical for low contact resistance and high wear resistance. Soft gold is not suitable for this purpose because it wears off quickly.

ELECTROLESS GOLD

In many instances where a process of electroless gold plating is desired, a capability is required of producing a pure, pore-free soft gold to a thickness much greater than that which can be achieved by a simple galvanic displacement process. The process must also be compatible with the photoresist present on the substrate. The classical baths containing borohydride or dimethylamineborane (DMAB) as the reducing agent (2, 27, 28) are *autocatalytic* and meet the first requirement, but commonly used positive photoresists are not stable in those baths because of the presence of cyanide and high alkalinity. For these reasons, recent efforts have been focused on the development of non-cyanide baths which can be operated at a near-neutral or acidic pH. In this section we only review the current status of development of such non-cyanide baths. For a more comprehensive review of various electroless gold processes, the reader is referred to the book chapters written by one of the present authors (2, 27, 28, 29).

Gold salts other than the Au(I)-cyanide complex used to formulate electroless gold baths include Au(I)-sulfite, Au(I)-thiosulfate, Au(I)-thiomalate, Au(III)-chloride, and Au(III)-phosphate complexes. Among them, the baths containing one or both of the first two complexes have been investigated most extensively, and they will be reviewed briefly below.

Sulfite Baths

The gold(I) sulfite complex, which has been in use for electroplating soft gold, has also been used to formulate electroless gold baths. Reducing agents investigated include hypophosphite, formaldehyde, hydrazine, borohydride and DMAB (30-34) as well as less common reducing compounds such as thiourea, methyl thiourea, and acetyl thiourea (35). These systems require the addition of a stabilizer for practical use. The following stabilizing agents are reported to be effective: 1,2-diaminoethane with KBr (30-33), ethylenediamine (34, 35), ethylenediamine tetraacetic acid (EDTA) (30-33), triethanolamine (36), nitrilotriacetic acid (36), and sodium thiosulfate (36). Using ascorbic acid as the reducing agent, Kato *et al* (37, 38) showed that the Au(I) sulfite complex can be reduced to gold autocatalytically, but the deposition rate was very low. They found that the deposition rate can be increased greatly by adding thiosulfate as the second complexing agent. The mixed ligand system will be described in the section after the next below.

Thiosulfate Bath

The use of an Au(I)-thiosulfate complex for electroless gold plating is only a recent development. Sullivan, Patel and Kohl (39) made an extensive electrochemical study of the cathodic reduction of $[Au(S_2O_3)_2]^{3-}$ and the anodic oxidation of various reducing agents at a gold electrode. They showed that, among a number of reducing agents investigated, ascorbic acid is the only compound that is electrocatalytically oxidized at a reasonable rate within the potential range of the reduction of the Au(I)-thiosulfate complex at a pH between 6.4 and 9.2 at room temperature. They thus formulated the electroless gold bath with the composition listed in Table 3. In this system the accumulation of free $S_2O_3^{2-}$ ions from the reduction of $[Au(S_2O_3)_2]^{3-}$ decreases the plating rate. Sullivan and Kohl (40) found that hydrogen peroxide reacts with free $S_2O_3^{2-}$ to form trithionate ($S_3O_6^{2-}$) and sulfate (SO_4^{2-}) ions, and this reaction can be utilized to maintain a constant plating rate through periodic addition of H_2O_2 into the bath. This bath has only a short life (<2 hr), which needs to be improved for practical purposes.

Table 3 *Electroless gold plating bath with Au(I) thiosulfate and ascorbic acid (39)*

$Na_3Au(S_2O_3)_2$	0.03 M
Na L-ascorbate	0.05
Citric acid	0.4
pH (KOH)	6.4
Temperature	30°C
Plating rate	0.76 μm hr^{-1}

Table 4 *Thiosulfate-sulfite mixed ligand baths with various reducing agents*

		Reducing agent			
Bath constituent	Thiourea (42)	Ascorbic acid (38)	Ascorbic acid (47)	Hypophosphite (45)**	Hydrazine (46)
$NaAuCl_4$	0.005-0.025 M	0.01 M		0.0025 M	
$Na_3Au(SO_3)_2$			0.006 M		
$(NH_4)_3Au(SO_3)_2$					0.01M
Na_2EDTA					0.25
Na_2SO_3	0.04-0.2	0.08-0.32	0.1	0.05	
$Na_2S_2O_3$	0.2-0.6	0.08-0.32	0.1	0.05	0.063
$Na_2B_4O_7$	0.066-0.13				
Na_2HPO_4		0.05-0.2			
NH_4Cl			0.05		
Boric acid				0.16	
K tartrate					0.13
Hydroquinone	0.0018-0.018				
Mercaptobenzothiazole		Trace			
Stabilizer			0.1-100ppm*		
Dimethylamine					0.067
2-Chloromethylquinoline					10ppm
Tl_2SO_4					3ppm
Reducing agent	0.0013-0.013	0.05-0.2	0.25	0.075	0.36
pH	7.5-8.5	7.5	6.0	7.5	6.5
Temperature	60-90°C	60°C	60°C	70°C	60°C

* See text for compounds.

** Bath made up by mixing equal parts of two solutions followed by adding reducing agent. For details, see the original reference (45).

Thiosulfate-Sulfite Mixed Ligand Bath

The non-cyanide baths described above containing either sulfite or thiosulfate as a sole complexing agent appear to have insufficient stability. Baths containing both thiosulfate and sulfite are more stable, and those containing thiourea (41-43), ascorbic acid (37, 38, 44), hypophosphite (45), or hydrazine (46) as the reducing agent have been developed. Examples of bath compositions and operating conditions are summarized in Table 4.

The thiourea bath was developed and subsequently improved by a group of investigators at Hitachi Ltd. In this system, thiourea undergoes complex chemical reactions through the formation of a radical intermediate, $(NH)(NH_2)CS\cdot$, to form final products including urea (a major product) and dicyandiamine. This radical intermediate reacts with dissolved oxygen in the bath to form formamidine sulfinic acid, $(NH_2)_2CSO_2$, which is believed to be responsible for bath instability. Hydroquinone, listed in Table 4, reacts with the radical intermediate before it produces the undesirable compound. It is also of interest that the reaction between hydroquinone and the radical intermediate regenerates thiourea. Thus, hydroquinone acts as a stabilizer as well as a recycling agent for thiourea. This bath is now commercially available.

The ascorbic acid bath was developed at Kanto Chemical Co of Japan. This bath contains a minute amount of stabilizer, 2-mercaptobenzothiazole (MBT), which increases the bath life from only three hours to more than 35 hours without affecting the plating rate, which is of the order of 1 $\mu m\ hr^{-1}$. This plating rate can be increased by using certain additives. For example, the addition of 0.005M of ethylenediamine increases it by a factor of three. The Tl^+ ion is also an effective accelerator. The addition of only 1 ppm of Tl^+ doubles the rate. The acceleration effect of Tl^+ has been shown to be due to its depolarization effect on the partial cathodic reaction brought about by the so-called underpotential deposition (UPD) of Tl on gold. The effect is similar to what is known for the classical cyanide system. This bath is also commercially available.

More recently, Honma and coworkers (47, 48) made an extensive investigation of the ascorbic acid bath. They found that the addition of nitrilotriacetic acid improves the stability of the Au(I)-sulfite complex through the formation of a complex which is more

stable with respect to the disproportionation reaction of Au^+. To improve the stability further, other compounds such as $K_4Fe(CN)_6$, $K_2Ni(CN)_4$, 2,2'-dipyridyl, and cupferron can be added at a concentration between 0.1 and 100 ppm. It is reported that the bond strength between gold wire and the deposit was much greater when the bath contained $K_2Ni(CN)_4$ or cupferron rather than 2,2'-dipyridyl. This difference was attributed, not to impurity or surface morphology, but to crystal orientation. The deposits with good bondability had (220) and (311) preferred orientations. Another significant finding reported by these authors is that the addition of hydrazine as a second reducing agent increases the plating rate by a factor of up to two. A plating rate of 1.7μm hr^{-1} was achieved at pH 6 and 60°C.

A hypophosphite bath containing both sulfite and thiosulfate was developed by Paunovic and Sambucetti (45) as a result of an extensive electrochemical investigation of various baths containing different reducing agents. It was concluded that the mixed ligand system combined with hypophosphite gives the most satisfactory performance in terms of bath stability and plating rate. Their bath is prepared by mixing equal parts of two solutions, and the composition of the bath after makeup is listed in Table 4. The plating rate achieved at pH 7.5 and 70°C was 0.9μm hr^{-1}. The bath is stable for about 10 hr, but it can be extended by the addition of a stabilizer such as SCN^-. (See also the next section below) No sulfur was detected in the gold; and good bondability of gold wire to the deposit was confirmed.

Shiokawa *et al* (46) used hydrazine as the reducing agent in their sulfite-thiosulfate bath. An example of the bath composition is given in Table 4. The bath contains many different additives for a variety of reasons. They include a strong complexing agent such as EDTA to mask metallic impurities, *eg*, Cu^{2+} and Ni^{2+}, an amine such as triethanolamine or ethylenediamine to suppress the formation of gas pits, a quinoline derivative such as 2-chloroquinoline to prevent extraneous gold deposition on photoresist, a salt of citrate or tartrate to stabilize the bath, and As^{3+}, Tl^+, or Pb^{2+} to improve plating uniformity. The bath given as an example in Table 4 plates 0.93μm in one hour when operated at pH 6.5 and 60°C.

Recently, Krulick and Mandich (49) discovered that the Au(I) sulfite-thiosulfate mixed ligand system functions as an autocatalytic bath without adding any conventional reducing agent. Such bath was found to plate 0.03 to 0.3μm of gold in 15 min at pH 6.5 to 9.0 and 55 to 75°C directly on electroless nickel. The inventors believe that the sulfite-thiosulfate mixture itself is a reducing agent system, and that especially sulfite functions as the main reducing agent in this bath. The bath is completely stable for more than ten replenishment cycles over the period of many months. The inventors also describe (50) that the plating rate can be increased by adding an amino acid such as glycine. They obtained 0.4 to 1.0μm of gold in 10 min using such a bath.

Sulfite-Thiocyanate Mixed Ligand Bath

Kawashima and Nakao (51) developed a bath containing sulfite and thiocyanate in place of thiosulfate as mixed ligands. They also used ascorbic acid as the reducing agent. The bath contained 0.01M $HAuCl_4$, 0.1M Na_2SO_3, 0.1M KSCN, and 0.1M ascorbic acid, and it was operated at pH 6.0 and 60°C. The plating rate was 0.5 μm hr^{-1}. It decreased with increasing concentration of Na_2SO_3 and increased with increasing KSCN concentration. The bath exhibited good stability during two to three temperature cycles consisting of heating at 60°C for 6 hr and standing at room temperature for 18 hr, including the period of natural cooling. Good wire bondability is reported for a 0.5μm thick gold film obtained from this bath.

CONCLUDING REMARKS

The unique physical properties of gold have made it an indispensable material in the electronics manufacturing industry. Both electroplated soft and hard golds have been in extensive use for more than 30 years. Soft gold will continue to be used, with non-cyanide baths finding an increasing share in the future. Hard gold can be plated only with traditional cyanide-based baths at present. Palladium-based alternative finishes for connector contacts with a thin top layer of hard gold will find an increasing market share in the future as their technical advantages become more widely recognized. Autocatalytic electroless gold plating has also been known for more than 25 years. With the recent introduction into the market of non-cyanide, neutral pH baths, electroless gold will find an increasing number of applications where its advantages over electroplating are recognized with proper understanding of its limitations. However, it appears necessary to continue to study the cause of the limitations and to improve currently available processes in order for electroless gold to be accepted with greater confidence by the electronics industry.

It is hoped that this short review will be helpful in obtaining an overall picture of the current status of various gold plating processes used in the electronics industry.

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